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A FIELD EXPERIMENT TO PARTITION THE EFFECTS OF DRY AND
WET DEPOSITION ON METALLIC MATERIALS

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16. ABSTRACT At a material exposure site located at the Research Triangle Park, NC the Environmental Protection Agency began in 1982 a study to partition the effects of dry and wet deposition on galvanized and weathering steel panels. At the site, air quality and meteorological parameters are continuously measured and reported as hourly averages. The concentration and chemistry of particles and the amount of rainfall and chemistry are also recorded. In this study a mobile device covers a set of panels only during each rain event. Another set of panels is exposed uncovered at the site. The panels are exposed and cleaned according to standard ASTM procedures. After two years of exposure the weight-loss of the galvanized steel for the uncovered exposure was nearly twice the weight-loss recorded for the covered condition. Whereas, for the weathering steel, the weight-loss for the covered exposure is greater than the uncovered exposure. Wet deposition (rainfall) has a beneficial effect on the corrosion of weathering steel, while having a detrimental effect on galvanized steel by removing the protective CaCO_3 film. In order to further investigate the effects of wet deposition on these materials another covering device that not only prevents rain from falling on exposed sets of panels but sprays the panels with a known volume and pH of water is being installed at the site.		
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INTRODUCTION

At a material exposure site located at the Research Triangle Park, N.C., the Environmental Protection Agency began in October 1982 a study to partition the effects of dry and wet deposition on galvanized steel and Corten A weathering steel. In this study a mobile device covers a set of the metallic materials during each rain event. Another set of the metals is boldly exposed (uncovered) at the site. The results of the two-year exposure of these two metals is presented.

EXPERIMENTAL PROCEDURES

Panels (10 x 15 cm) of 20 gauge galvanized steel and Corten A weathering steel were prepared. Each panel was identified by a code stenciled lightly on the ground exposed side of the panel. Prior to field exposure the galvanized panels were cleaned by immersion for 2 minutes in 10% by weight of ammonium chloride solution at a temperature of 60-80°C (1). The weathering steel panels were cleaned by immersion in Clark's solution (1). All panels were rinsed in deionized water and then with methanol to remove moisture, and weighed to 0.1 mg.

The panels were exposed at 30° between ceramic insulators facing south at the site (2). Panels of each metal were exposed in triplicate for periods of 6, 12, and 24 months. The six-month panels were continually replaced with cleaned panels in order to study the corrosion during winter and summer exposures. Two sets of each metal panels were exposed at the site. An automatic device (Figure 1) which is triggered by a sensor on a rain bucket collector covered one set of panels only during each rain event. This set of panels is exposed primarily to dry deposition. The remaining set of panels

was exposed uncovered to wet and dry deposition. After each exposure period the panels were removed, then cleaned according to the procedure established prior to the exposure and reweighed to 0.1 mg.

RESULTS

Weight-loss data for the galvanized and weathering steel for the covered and uncovered conditions are shown in Table 1 for each exposure period. The differences in weight-loss (Δ loss) for covered and uncovered conditions are also shown in the table. After the initial six-month exposure period, the identity code of the weathering steel panels was not readable and new panels were prepared and exposed. The weight-loss of the unidentified panels was determined as the difference of the combined weight of the triplicate panels for each exposure period. This data is reported in Table 1 without computation of a standard deviation.

After two years of exposure the weight-loss of the galvanized steel for the uncovered exposure is nearly twice the weight-loss recorded for the covered condition. Whereas, for the weathering steel, the weight-loss for the covered exposure is greater than the uncovered exposure.

DISCUSSION

During exposure, galvanized steel and weathering steel are expected to corrode by forming a protective surface film that retards corrosion. The rate of corrosion would then be diffusion controlled and depend upon the thickness of the film. Many of the corrosion products, particularly the carbonates, hydroxides, etc. within the film are soluble in acid solutions. In environments where increased acidity is present, dissolution of the protective film is a competing mechanism that accelerates the rate of corrosion of metals.

Previous exposure studies of these metals have shown that time-of-wetness and SO_2 concentrations contribute to the accelerated corrosion (3)(4). At the Research Triangle Park, NC exposure site, the ambient concentration of SO_2 is below the detectable limit (5 ppb) of air monitoring instrumentation and is not significantly different from zero. At these levels dry deposition of SO_2 is not expected to be an important factor in the corrosion of these metals. Time-of-wetness results from both the formation of dew and rain. With very low SO_2 levels, the dew is not expected to be very acidic. The average pH of the rain at the site is about 4.5, however, specific rain events may have lower pH values.

The environmental rain data acquired at the site were compiled in Table 2 for each exposure period. Simple linear regression analysis was performed using each of the factors as the independent variable and the difference in erosion (Δ loss in Table 1) as the dependent variable. All of the regression coefficients were significant. The coefficients for the amount of rainfall was considered to be the most important, since delivery of SO_4^{2-} , NO_3^- and H^+ (concentrations relatively constant) to the surface of the metals is dependent of rainfall.

In a clean environment, the corrosion film that forms on galvanized steel consist primarily of ZnCO_3 . This process is consistent with the non-linear time function that has been observed for the corrosion of zinc (5). In pure water ZnCO_3 is reported to dissolve at 15°C to saturation at a rate of .001 gms per 100 grams or 1 mg per 100 cm^3 . This would be equivalent to .01 $\text{mg}/\text{cm}^2/\text{cm}$ rain. Thus, a theoretical saturation coefficient for pure rain at 15°C would be .0052 mg per cm^2 per cm. The Research Triangle Park rain coefficient for galvanized steel is 0.00360 ± 0.00052 mg per cm^2 per cm. Although ZnCO_3 is more soluble in acidic solutions than in pure water, the

amount of time rain is in contact with the surface of the galvanized steel panel is not expected to be long enough for the solution to become saturated. The magnitude of the regression coefficient is reasonable for a film dissolution mechanism. Thus, wet deposition (rainfall) is removing the protective film on the uncovered galvanized steel at the site.

In a recent study of weathering steel, Haynie reports a regression coefficient for rain of $-0.0798 \pm 0.0227 \mu/\text{cm}$ or $-0.061446 \pm 0.017479 \text{ mg per cm}^2 \text{ per cm}$ (4). In this study the dissolution of the oxide film that forms on weathering steel is reduced by the amount of rainfall. The rain coefficient for weathering steel obtained from the Research Triangle Park exposure study is $-0.03442 \pm 0.01814 \text{ mg per cm}^2 \text{ per cm}$. The values of these two coefficients are not significantly different at the 95% confidence level using a t test. Thus, wet deposition (rainfall) has a beneficial effect on the corrosion of weathering steel, while having a detrimental effect on galvanized steel.

Long-term corrosion studies of weathering steel indicate that the corrosion time function should be nearly parabolic (6)(7). This function is associated with the formation of a passive protective film. It is apparent that two-year data are not sufficient to accurately predict long-term behavior.

CONCLUSION

The mobile covering device appears to provide a means to partition the effects of dry and wet deposition during field exposure of metallic materials. Wet deposition (rainfall) is having an effect on the weathering of galvanized and weathering steels. In order to investigate the effects of wet deposition on these materials, mobile covering devices that not only prevent rain from falling on exposed materials but sprays the materials with a known volume and

pH of dionized water are being installed at the RTP, NC and Steubenville, Ohio exposure sites. The Ohio site has higher ambient SO₂ concentrations than the RTP site. These devices should provide the means to not only partition the effects of wet and dry deposition on materials but the effects of clean and ambient rainfall (wet deposition).

Table 1. Weight-Loss Data (mg/cm²) of Exposed Metals

Exposure Period	Galvanized Steel			Weathering Steel		
	<u>Covered</u>	<u>Uncovered</u>	<u>ΔLoss</u>	<u>Covered</u>	<u>Uncovered</u>	<u>ΔLoss</u>
6 Months						
10/82- 5/83	.33+.04	.52+.04	.19	20.6	23.4+1.3	2.8
5/83-11/83	.37+.06	.44+.05	.07	19.4+.05	18.3+1.3	-1.1
11/83- 5/84	.44+.11	.65+.14	.21	20.7+3.2	16.5+.3	-4.2
5/84-11/84	.27+.02	.54+.03	.27	19.8+0.1	18.6+.3	-1.2
12 Months						
10/82-11/83	.47+.01	.94+.06	.47	30.3	21.3	- .9
18 Months						
5/83-11/84	-	-	-	33.7+3.6	28.4+3.4	- .5
24 Months						
10/82-11/84	.82+.01	1.66+.09	.84	44.7	37.5	- .7

Table 2. Environmental Rain Data

Exposure Period	Rainfall(cm)	SO ₄ (N moles/cm ²)	NO ₃ (N moles/cm ²)	H(N moles/cm ²)
6 Months	65.3	877.0	774.0	1436.0
	46.3	1334.0	1097.0	2943.0
	80.7	1014.0	879.0	2082.0
	50.2	1045.0	1000.0	2194.0
12 Months	111.0	2212.0	1872.0	4378.0
18 Months*	192.3	3226.0	2751.0	6460.0
24 Months	242.4	4271.0	3752.0	8655.0

*For weathering steel only.

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